

Crystal Growth: Physics, Technology and Modeling

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Lecture 13. Growth modeling in microscale

<http://www.unipress.waw.pl/~stach/cg-2021-22>

Growth modeling – two approaches

- **Modeling in macroscale**
 - transport processes during growth (mass, energy, momentum)
 - strain in nonuniform structures
 - electric properties of electronic structures and devices
 - optical properties of optoelectronic structures and devices
 - crystal morphology
- **Modeling in atomic scale**
 - crystal structure
 - energetic properties
 - kinetic properties
 - optical transitions

Growth modeling – methods

- **Modeling in macroscale**
 - finite difference
 - finite volume
 - finite element
- **Modeling in atomic scale**
 - Monte Carlo
 - molecular dynamics
 - ab initio – density functional theory (DFT)

Monte Carlo method

- **Determination of the space of elementary events**
- **Random variable definition**
- **Determination of random variable probability distribution**
- **Sampling**
- **Determination of physical quantities**

Monte Carlo method – space of the events

Axiomatic definition of probability

Probability - measure p , defined on the set (algebra) of random events $\{A_i, i = 1, 2, 3, \dots, n\}$, satisfying the following relationships :

- $p(\emptyset) = 0, \quad p(E) = 1$
- $0 \leq p(A) \leq 1$
- $p(A \cup B) = p(A) + p(B) \quad \Rightarrow \quad \text{excluding events } A \cap B = \emptyset$

Conditional probability, i.e. A occurs provided that B occurred, is :

$$P(A|B) = \frac{P(A \cap B)}{P(B)}$$

Random variable

- Algebra $\{A\}$ of random events is projected on real function. Such function is called random variable

$$X: \{A\} \Rightarrow R$$

- Algebra $\{A\}$ has probability defined, according to the above listed 3 axioms.

$$p: \{A\} \Rightarrow [0, 1]$$

Any value of random variable could be associated with the probability equal the sum of the probabilities of exclusive events for which random variable has the value X . The inverse dependence of the probability on the random variable is called probability distribution.

Probability distributions

- Positively defined

$$p(x) \geq 0$$

- Normalized

$$\sum_i p(x_i) = 1$$

- Could be determined by measurements, e.g. energy E

$$p(E_k) = \frac{n_k}{N}$$

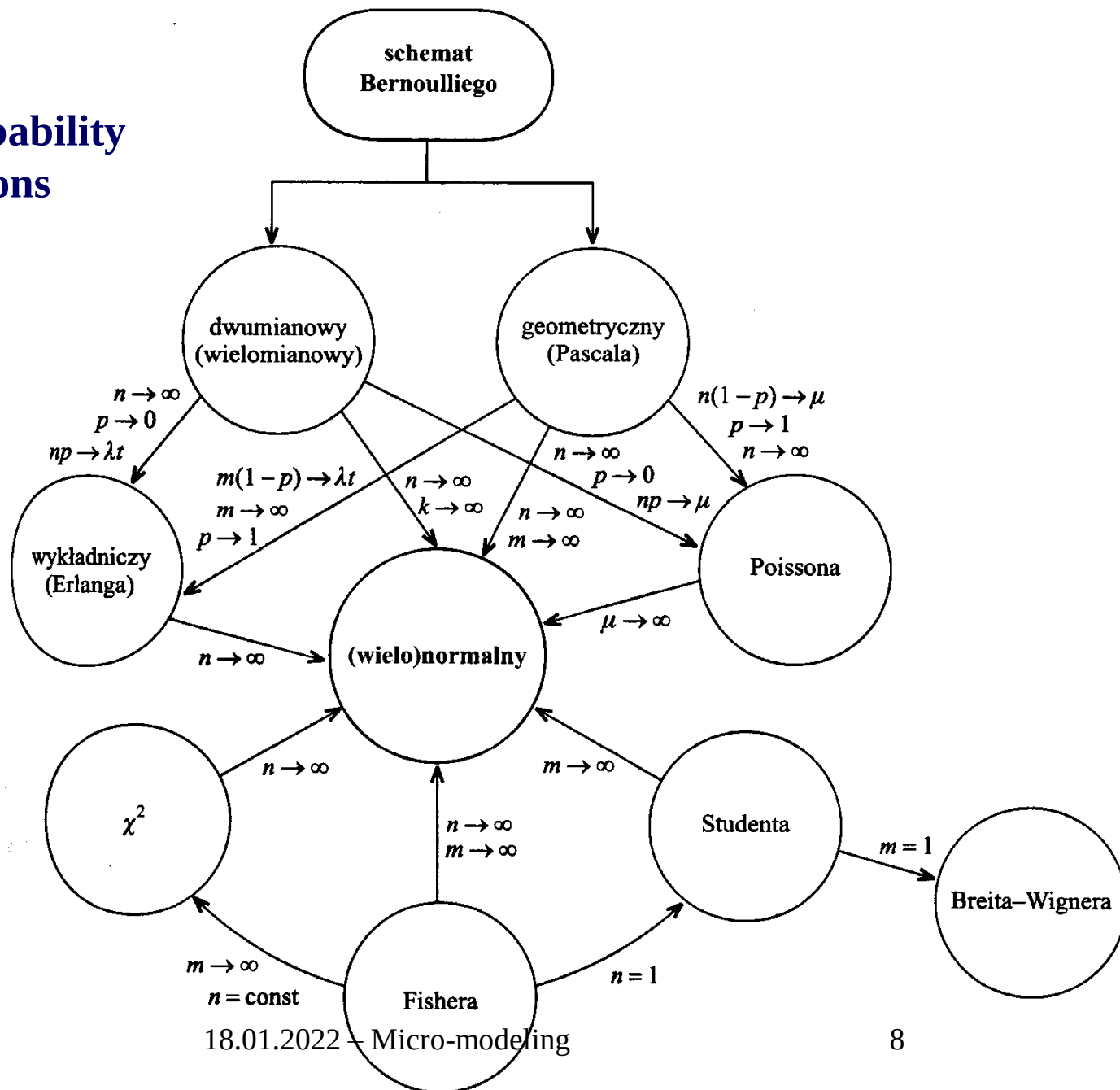
where: n_k – number of particles within $[E_k, E_k + \Delta E]$ interval, N – total number of particles.

- Continuous and discrete distributions

Probability is called discrete when has finite number of values.

Different probability distributions

$$\int_{-\infty}^{\infty} f(x) dx = 1$$



Sampling

Sampling – generation of random numbers of a given probability distribution of random variable (x) using numbers having uniform probability distribution (ξ).

Condition – equality of probability (equality of distributions):

$$p(x < y) = p(\xi < \xi_o) \qquad F(y) = F(\xi_o)$$

where

$$F(y) \equiv p(x < y) = \int_{-\infty}^y f(x) dx$$

Uniform probability distribution

$$f(\xi) = \begin{cases} 1 & \xi \in [0, 1] \\ 0 & \xi \notin [0, 1] \end{cases}$$

Sampling equation

$$\int_0^{\xi_o} d\xi = \xi_o = F(y) = \int_{-\infty}^y f(x) dx \quad \Rightarrow \quad y = F^{-1}(\xi_o)$$

Sampling

Sampling equation

$$y = F^{-1}(\xi_o)$$

Example – Lorentz distribution

$$f(x) = \frac{1}{\pi} \frac{1}{1 + x^2}$$

Lorentz random variable y

$$\int_{-\infty}^y \frac{dx}{\pi(1 + x^2)} = \frac{\arctan(y)}{\pi} + \frac{1}{2} = \xi_o \quad \Rightarrow \quad y = \tan\left(\pi\xi_o - \frac{1}{2}\right)$$

Equilibrium systems (huge phase space)

- Uniform sampling
- Importance sampling

Uniform sampling - rejection techniques

Distribution function in [0,1] interval:

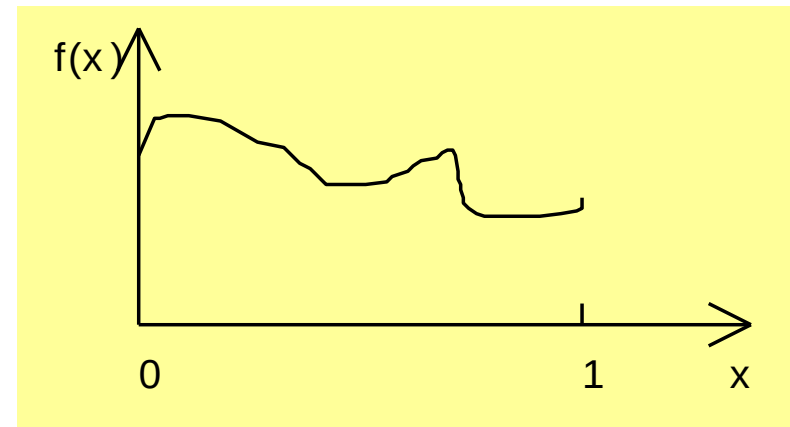
$$\int_0^1 f(x) dx = 1$$

Sampling by rejection technique:

- Generation of random number ξ_1 :
- Generation of random number ξ_2 :
- Verification condition

$$\xi_2 < \frac{f(\xi_1)}{\max(f)} \Rightarrow x = \xi_1$$

- Weakly convergent – large noise
- Reliable (no systematic error)



Metropolis algorithm – importance sampling

Metropolis et al , J. Chem. Phys. 21 (1953) 1087

Equilibrium distribution – Gibbs canonic ensemble:

$$f(\mathbf{p}, \mathbf{q}) = Z^{-1} \exp\left(-\frac{E(\mathbf{p}, \mathbf{q})}{kT}\right)$$

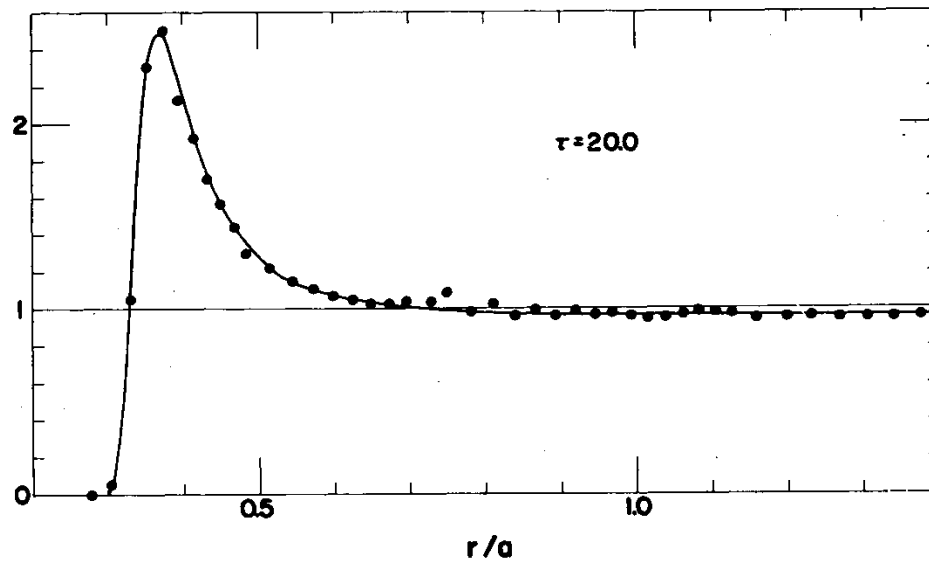
- Initial state $\mathbf{q}(t)$
- Next state $\mathbf{q}'(t+1)$
- Transition probability Q
- $Q > 1$ accepted
- $Q < 1$ generation random number ξ , when $\xi < Q$ accepted, if not it does not

$$Q = \frac{f(\mathbf{q})}{f(\mathbf{q}')} = \exp\left[-\frac{E(\mathbf{q}') - E(\mathbf{q})}{kT}\right]$$

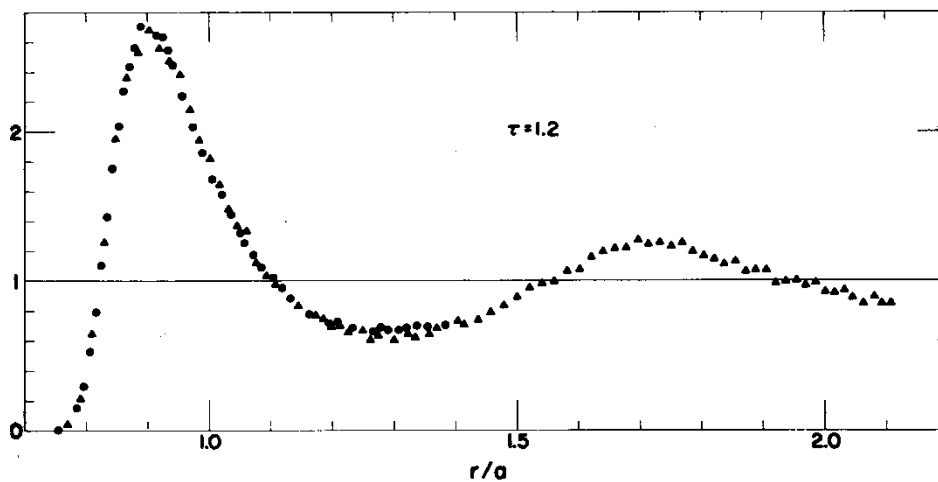
Metropolis algorithm – biased wandering in phase space

- Strongly convergent – low noise
- Unreliable (prone to systematic error)

Density – density correlation function

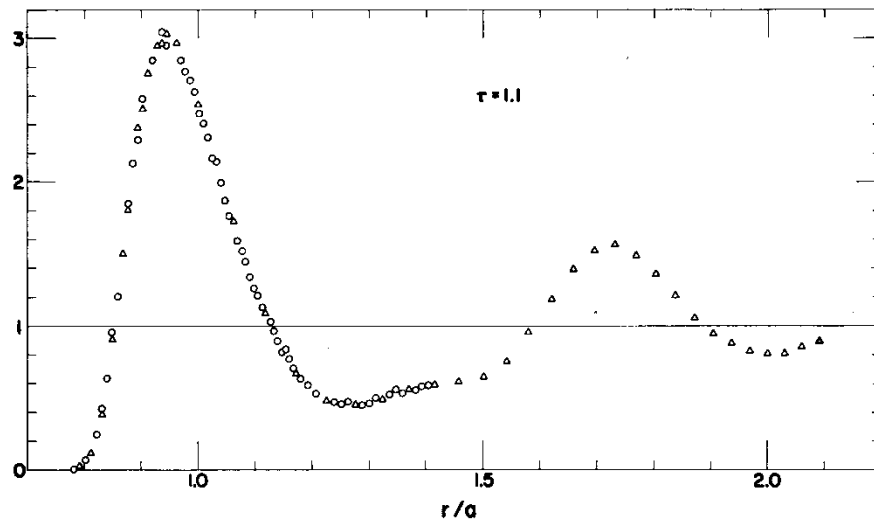


Vapor

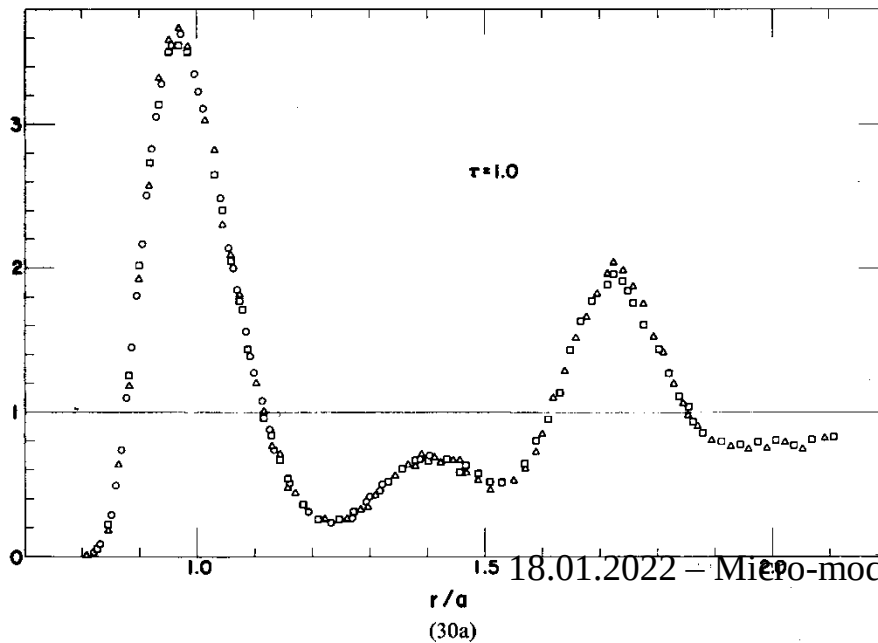


Liquid

Density – density correlation function - solid



Low density



High density

Molecular dynamics – time integration method

Hamilton formalism

$$\dot{q} = \frac{\partial H}{\partial p} \quad \dot{p} = - \frac{\partial H}{\partial q} \quad H(p, q) = \sum_i \frac{p_i^2}{2m} + V(\{q_i\})$$

Conservative forces $V = V(q)$

$$p = mv \quad m\dot{v} = F \quad \ddot{q} = \frac{F}{m}$$

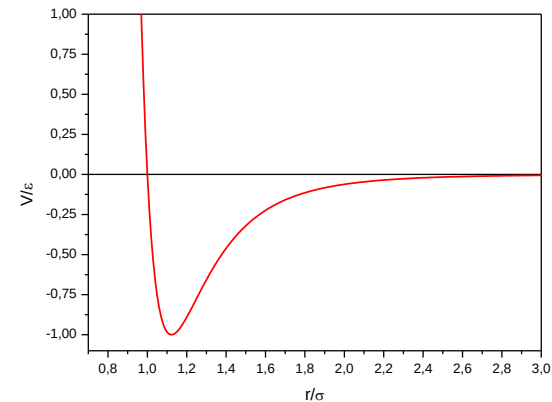
Molecular dynamics:

- Determination of interaction potential
- Integration of time evolution equation
- Averaging

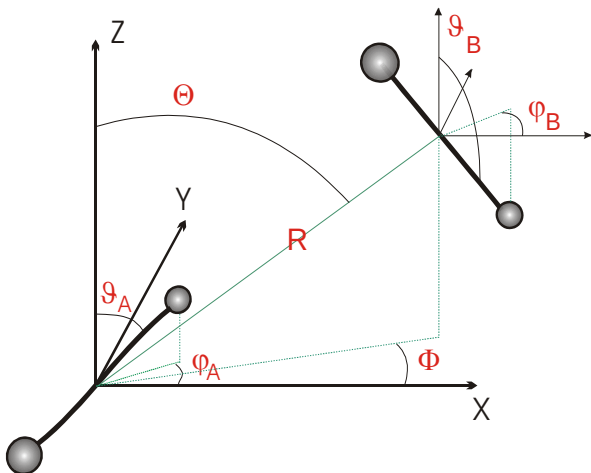
Interaction potentials

- Lennard- Jones potential (model)

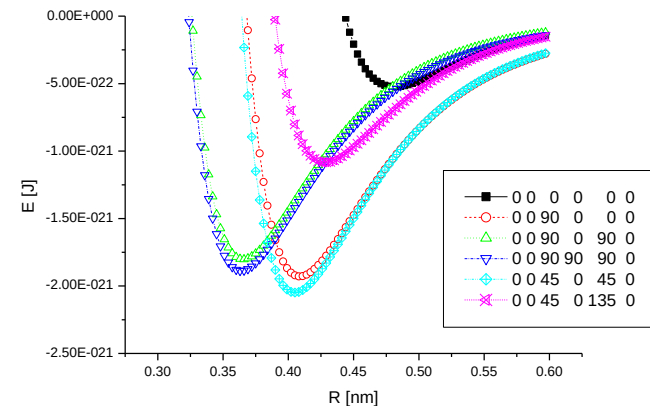
$$V(r) = \begin{cases} 4\varepsilon \left[\left(\frac{r}{\sigma} \right)^{-12} - \left(\frac{r}{\sigma} \right)^{-6} \right] & r < r_c \\ 0 & r > r_c \end{cases}$$



- Derived from QM calculations, e.g. N₂-N₂ potential



P. Strak – PhD (2006)



P. Strak et al. J. Chem. Phys. 126 (2007) 194501

Calculation of force – the time consuming action

Substances – interaction potentials

1. Noble gases - pairwise Lennard-Jones interactions (short range)
2. Ionic crystals – pairwise Coulomb interactions (long range)
3. Semiconductor crystals – triple interactions (short range)
4. Metals – collective interactions (short range)

Calculation of interaction potential is formidable task even at present:

- Extremely high precision
- Large number of configurations
- Large number of distances, angles, etc.

Integration of time evolution equation

Solution method – continuous change is represented by step-wise evolution

$$h = \Delta t = t_{n+1} - t_n$$

Open method – predictor method, e.g. Euler method Taylor series expansion

$$q_{n+1} = q_n + v_n h + \frac{1}{2} f_n h^2 \qquad v_{n+1} = v_n + f_n h$$

Fast but relatively unstable

Closed methods – predictor-corrector method, e.g. modified Euler method

Predictor

$$z_{n+1} = q_n + v_n h + \frac{1}{2} f_n h^2$$

$$f_n^* = \frac{1}{2} (f_n + f(z_n))$$

Corrector

$$q_{n+1} = q_n + v_n h + \frac{1}{2} f_n^* h^2$$

$$v_{n+1} = v_n + f_n^* h$$

Slower (two force determination), but relatively more stable

Verlet method - workhorse

Verlet method – Taylor series expansion: forward and backward

$$\begin{aligned}q_{n+1} &= q_n + q'_n h + \frac{1}{2} q''_n h^2 + \frac{1}{6} q'''_n h^3 + O(h^4) \\q_{n-1} &= q_n - q'_n h + \frac{1}{2} q''_n h^2 - \frac{1}{6} q'''_n h^3 + O(h^4)\end{aligned}\quad q' \equiv \frac{\partial q}{\partial t}$$

Adding both sides (velocity independent algorithm)

$$q_{n+1} = 2q_n - q_{n-1} + f(q_n)h^2$$

$$v_n = (q_{n+1} - q_{n-1})/2h$$

Leapfrog algorithm

$$q_{n+1} = q_n + v_{n+1/2}h$$

$$v_{n+1/2} = v_{n-1/2} + f(q_n)h$$

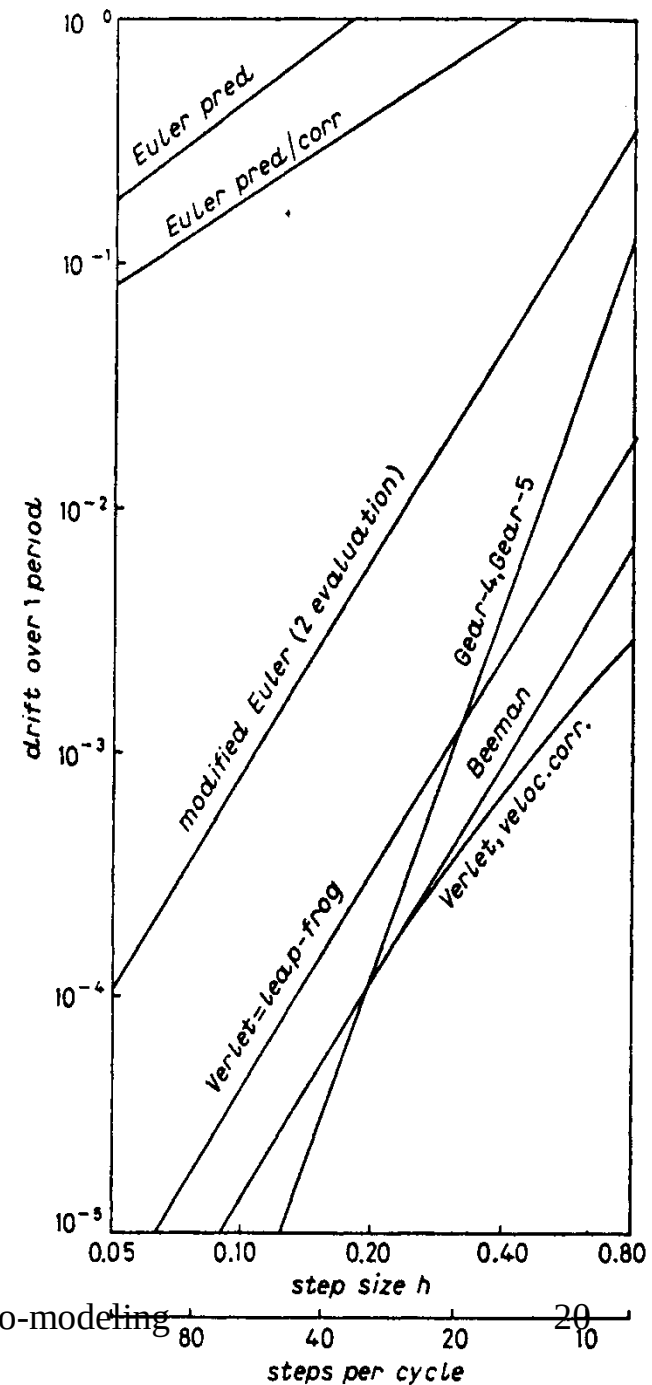
Verlet algorithm is stable, simple to implement, and of the cost of Euler method

Harmonic oscillator: coordinate comparison of various differentiation methods

Deviation from exact solution

Steps per cycle - i

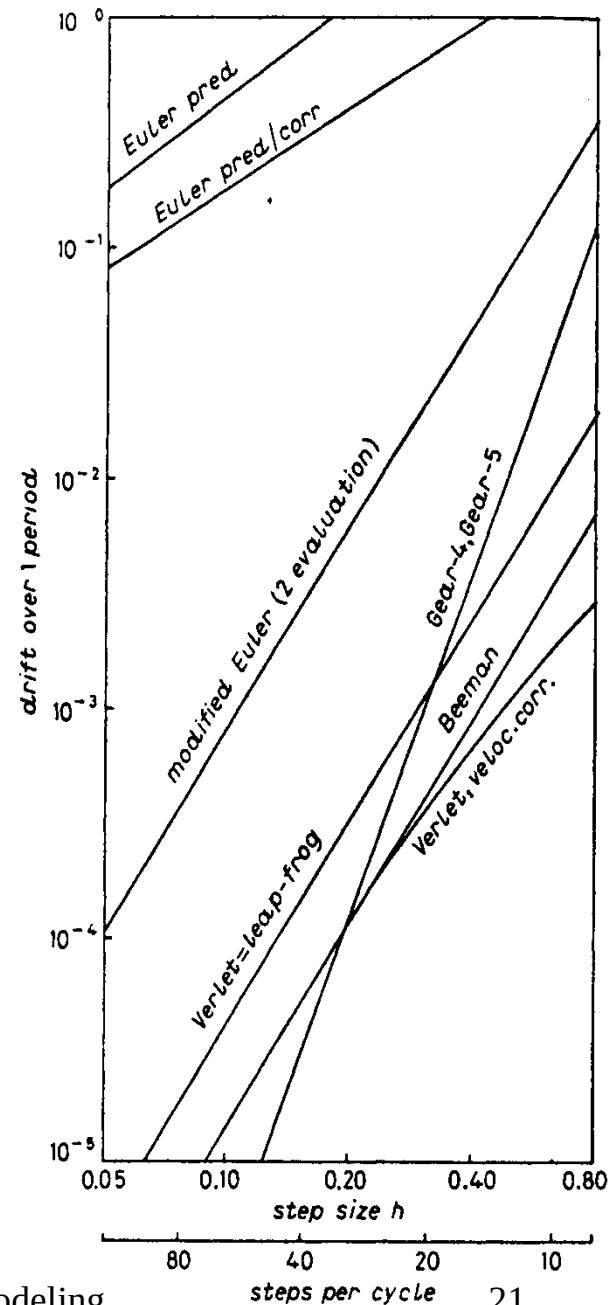
$$h = \frac{T}{i}$$



Harmonic oscillator: energy drift comparison of various differentiation methods

Steps per cycle - i

$$h = \frac{T}{i}$$



***Ab initio* methods – density functional theory(DFT)**

- **Hamiltonian (simplest spin-less case)**

$$\hat{H}(\vec{r}, \vec{R}) = - \sum_{\alpha} \frac{\hbar^2}{2M} \Delta_{R_{\alpha}} - \sum_i \frac{\hbar^2}{2m} \Delta_{r_i} + \sum_{\alpha < \beta} \frac{Z_{\alpha} Z_{\beta} e^2}{|R_{\alpha} - R_{\beta}|} \\ - \sum_{i, \alpha} \frac{Z_{\alpha} e^2}{|R_{\alpha} - r_i|} + \sum_{i, j} \frac{e^2}{|r_i - r_j|}$$

R, M – ionic coordinates & properties

r, m – electron coordinates & properties

- **Wavefunction of the system**

$$\Psi = \Psi(R, r)$$

Adiabatic & Born-Oppenheimer approximation is used to consider atomic nuclei motion classically

System energy

$$E(R) = T + E_{N-e} + E_{e-e} + E_{N-N}$$

- **Kinetic energy : T**

$$T = \frac{\left\langle \Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \left| -\sum_i \frac{\hbar^2}{2m} \Delta_{r_i} \right| \Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \right\rangle}{\langle \Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) | \Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \rangle}$$

Kinetic energy is not represented by the density functional.

- **Nuclei interaction energy: E_{N-N}**

$$E_{N-N} = \sum_{\alpha, \beta} \frac{Z_{\alpha} Z_{\beta} e^2}{|\vec{R}_{\alpha} - \vec{R}_{\beta}|}$$

Nuclei interaction energy does not depend on the electron density.

System energy

$$E(R) = T + E_{N-e} + E_{e-e} + E_{N-N}$$

- **Energy of electrons – nuclei interaction: E_{N-e}**

$$E_{N-e} = - \frac{\left\langle \Psi(\vec{r}_1, 2.. \vec{r}_N) \left| \sum_{i,\alpha} \frac{Z_\alpha e^2}{|\vec{r}_i - \vec{R}_\alpha|} \right| \Psi(\vec{r}_1, \vec{r}_2, \dots \vec{r}_N) \right\rangle}{\langle \Psi(\vec{r}_1, \vec{r}_2, \dots \vec{r}_N) | \Psi(\vec{r}_1, \vec{r}_2, \dots \vec{r}_N) \rangle}$$

Electron -nuclei interaction energy is functional of the electron density.

- **Energy of electron - electron interaction: E_{e-e}**

$$E_{e-e} = \frac{\left\langle \Psi(\vec{r}_1, 2.. \vec{r}_N) \left| \sum_{i,j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \right| \Psi(\vec{r}_1, \vec{r}_2, \dots \vec{r}_N) \right\rangle}{\langle \Psi(\vec{r}_1, \vec{r}_2, \dots \vec{r}_N) | \Psi(\vec{r}_1, \vec{r}_2, \dots \vec{r}_N) \rangle} = 2J - K$$

*J and K describe electron repulsion and correlation and exchange energy.
The repulsion energy is density functional the others are not*

Kohn-Sham equations

- System energy in external field $V_{\text{ext}}(\mathbf{r})$ is treated as functional of electron density $E[\rho]$, which attain minimum over the space of density created by normalized wavefunctions, i.e.:

$$\frac{\delta E[\rho]}{\delta \phi_i} = \epsilon_i$$

ϵ_j –Lagrange multiplier arising from normalization condition :

$$\langle \phi_i | \phi_j \rangle = \delta_{ij}$$

- Series of nonlinear, coupled equations for wavefunctions ϕ_j

$$\left\{ -\frac{\hbar^2}{2m} \Delta + V_{e-e} + V_{N-e} + V_{N-N} + V_{\text{Coul}} \right\} \phi_i = \epsilon_i \phi_i$$

Kohn-Sham equation in any base χ_j

- Wavefunction is expressed in the one-electron function base

$$|\phi_i\rangle = \sum_j c_{ij} |\chi_j\rangle$$

- Kohn-Sham equation are translated to array equation:

$$\sum_j H_{ij}(C) c_{jk} = \sum_j \epsilon_i S_{ij} c_{jk}$$

$$H_{ij} = \left\langle \chi_i \left| \left\{ -\frac{\hbar^2}{2m} \Delta + V_{e-e} + V_{N-e} + V_{N-N} + V_{Coul} \right\} \right| \chi_j \right\rangle \quad S_{ij} = \langle \chi_i | \chi_j \rangle$$

H depends on C, therefore this is nonlinear array equation that should be solved by the linear algebra methods as was explained.

Self-consistent field

- **Electron density**

$$\rho_{el}(\vec{r}) = \sum_i |\chi(\vec{r})|^2$$

- **Total charge density**

$$\rho_{tot}(\vec{r}) = \rho_{el}(\vec{r}) + \rho_{ion}(\vec{r}) = -e \sum_i f_{FD}(\varepsilon_i) |\chi_i(\vec{r})|^2 + e \sum_{\alpha} Z_{\alpha} \delta(\vec{r} - \vec{R}_{\alpha})$$

- **Fermi-Dirac distribution function**

$$f_{FD}(\varepsilon_i) = \frac{1}{1 + \exp\left(\frac{\varepsilon_i - E_F}{kT}\right)}$$

- **Poisson equation**

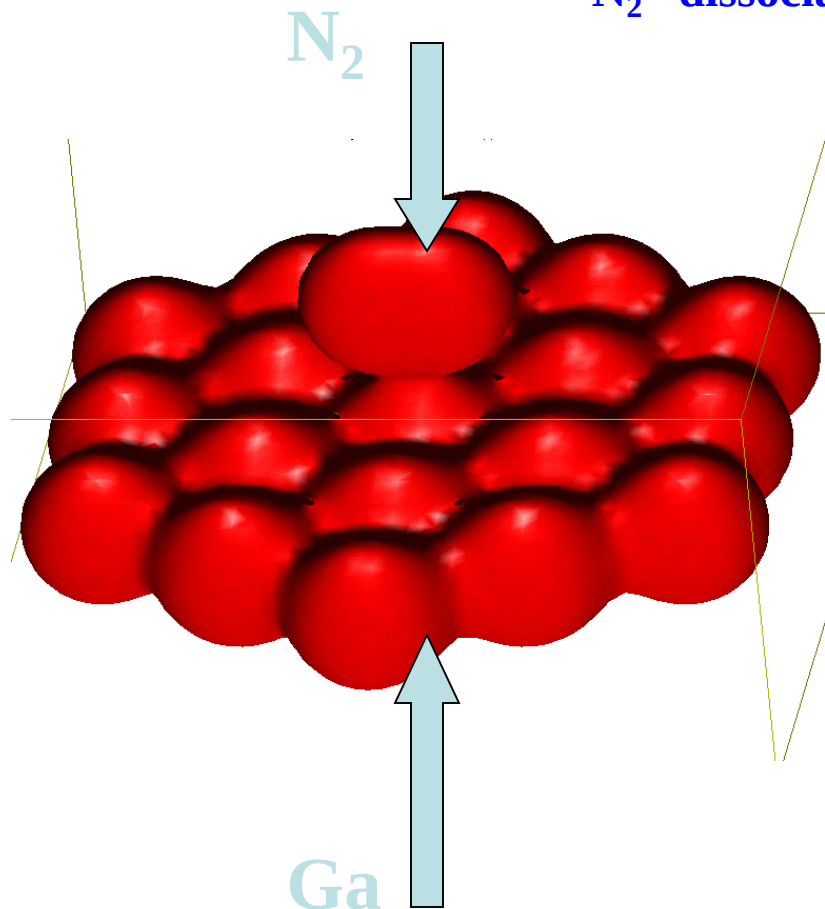
$$\Delta V_{Coul} = -\frac{\rho_{tot}}{\varepsilon_0}$$

Iteration equation solution (SCF loop)

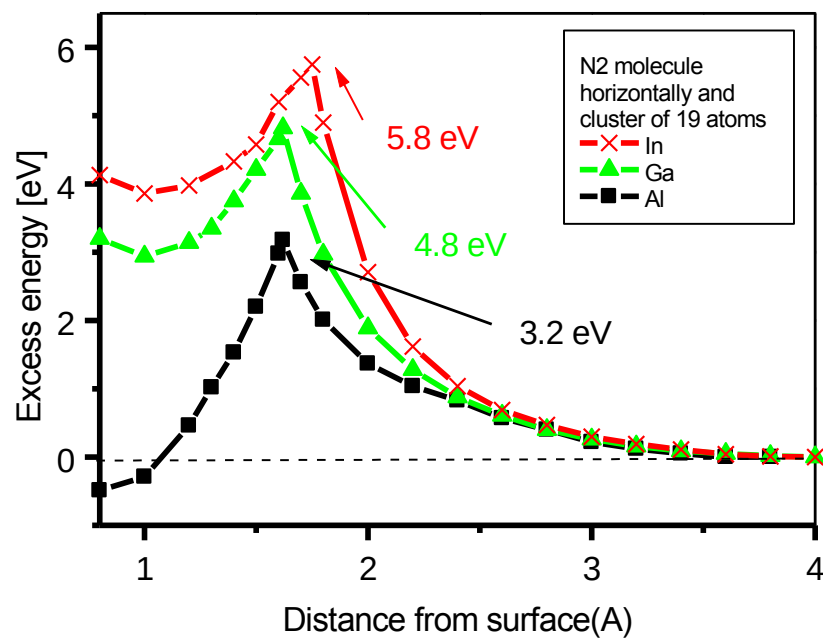
- I. Initial C_{ij} set**
- II. Calculate charge density**
- III. Solve Poisson equation**
- IV. Calculate H_{ij}**
- V. Solve Kohn-Sham equation – determine C_{ij}**
- VI. Determine Fermi energy from C_{ij}**
- VII. Calculate charge density**
- VIII. Determine convergence criterion**

N_2 - Ga(l) interaction

N_2 -dissociation energy - 9.8 eV



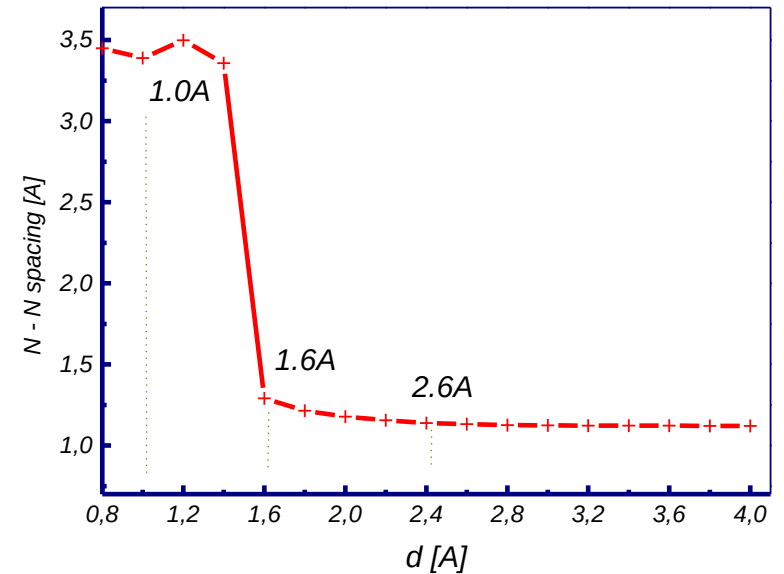
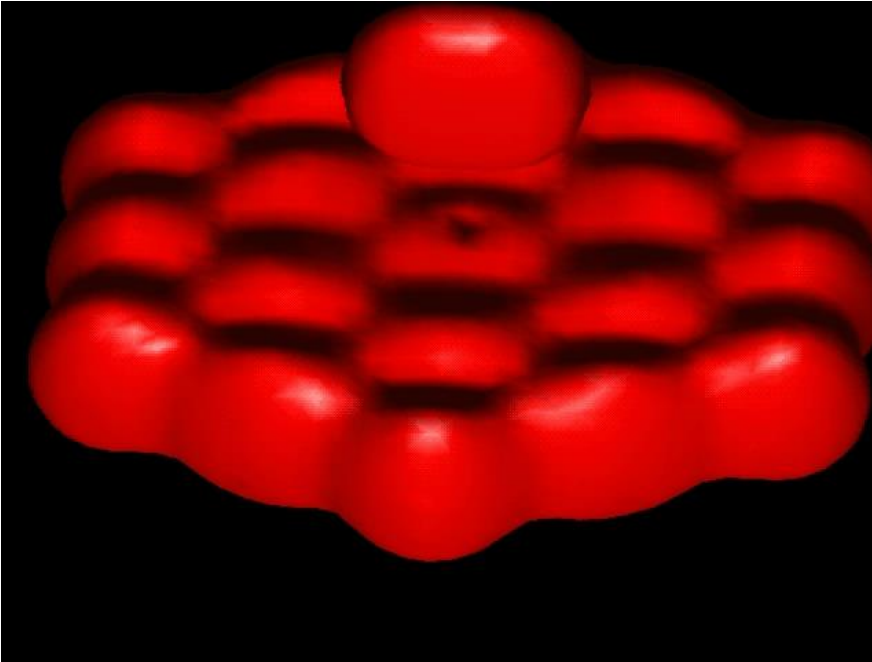
Excess energy of the system



Z. Romanowski - Dmol, DF-T

Z. Romanowski et al. *J. Chem. Phys.*
114 (2001) 6353

N_2 dissociation at Ga(l) surface



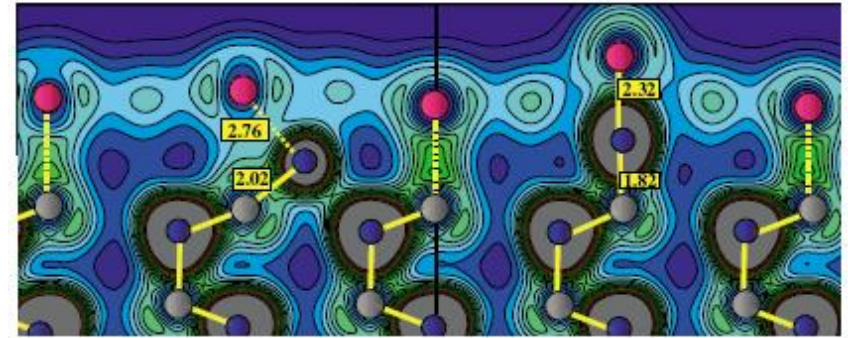
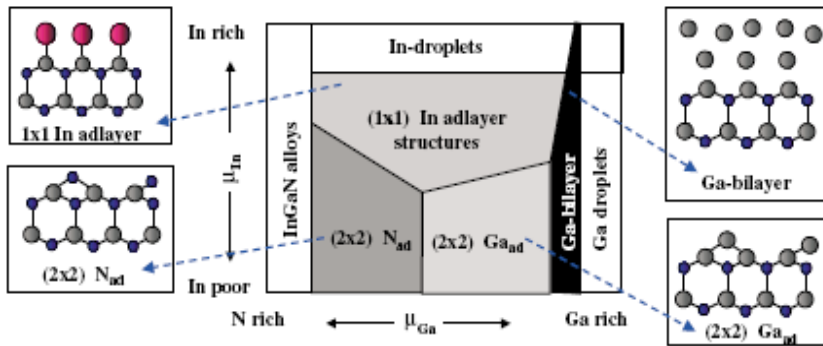
Z. Romanowski (PhD) - QM DFT

**Z. Romanowski et al. J. Chem. Phys.
114 (2001) 6353**

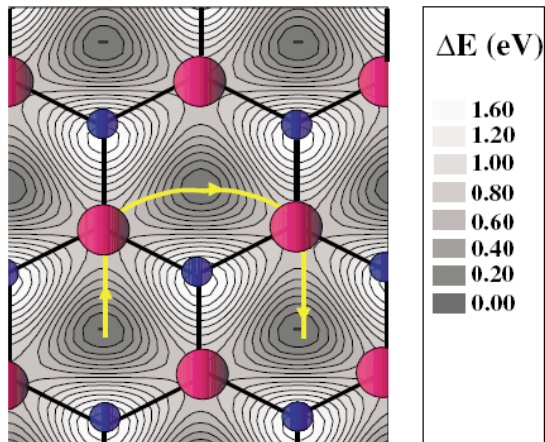
Diffusion of N at GaN(0001) surface : PA MBE

GaN (0001) surface – phase diagram

Gęstość ładunku elektronowego dla atomu N na powierzchni GaN (0001)



Energy surface for N adatom at In-covered GaN(0001) surface



Energia bariery na skok atomu N:
 - powierzchnia czysta – 1.3 eV
 - powierzchnia pokryta In – 0.05 eV

J. Neugebauer, et al. PRL 90 (2003) 056101

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